OTKA (NKFIH) K Grant - Report

Design, fabrication and analysis of luminescent silicon carbide nanocrystals for *in vivo* biomarker applications

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Project duration: **2012.01.01-2016.08.31.**

i. Objectives, budget and expected results in the research plan

The report starts with the word-by-word copy of the objectives in the research plan written in the beginning of 2011:
"The main goal of this project is to design, fabricate and analyze such semiconductor nanostructures which are *ab ovo* non-toxic for live cells and effectively applicable for biosensing at the same time. These nanostructures could be safely applied for *in vivo* detection and manipulation of biological molecules and open up new horizons for medical applications. The composition of the suitable nanostructures will be determined by atomistic simulations, and the desired nanostructures will be fabricated and analyzed. As was explained above semiconductor quantum dots (QDs) are used as fluorescent markers. The expected optical properties are i) high quantum yield ii) broad absorption spectra iii) but narrow photoluminescent emission. In addition, we prescribe that the host QDs should be bioinert, and should be resistant to both photobleaching and chemical degradation. For *in vivo* biological image applications it would be desirable to obtain relatively small QDs with diameter less than 6-7 nm and to possess near-infrared emission. We will study our fabricated QDs by such microscopes that are used in biological measurements and cytotoxicology tests will be applied on them in cooperation with the Institute of Enzymology of the Hungarian Academy of Sciences and the Department of Atomic Physics (DAP) at Budapest University of Technology and Economics."

This project was planned to be a highly multimodal both in terms in the diversity of applied methodologies – ranging from *ab initio* simulations through sample preparation to sophisticated analysis tools and biological tests – and number of groups in various institutions (Wigner RCP HAS, Research Institute for Technical Physics and Materials Science HAS, Institute of Enzymology HAS, Budapest University of Technology and Economics). The budget of the project was planned to mostly spent on chemicals and related materials, user's costs of large equipments (e.g., high resolution transmission electron microscope), and to pay one PhD fellowship to work full time on this project. In addition, investments were required on small equipments that were employed to prepare the samples. Furthermore, part-time work of laboratory assistants was also financed. The costs of participation at international conferences were financed by other sources.

As a production of the research we planned the following in 2011:
"In the first three years of the project we will publish at least one paper in a high impact journal in each year, while in the case of successful experiments at the end of this project the results will be published in a very high impact journal (similar to specialized Nature journal)."

ii. Personnel associated with the project

The project started at 2012 with one well-trained new PhD student, Dávid Beke, whose salary was financed by the project. The quality of his work reached rapidly the quality of a well-trained Postdoc (see also Section iv). Later on we involved Gyula Károlyházy in the research as an MSc student who continued with us as a PhD student from 2014. Later on Gabriella Drávecz also worked part-time on this project as a Postdoc researcher from 2015. Regarding the theory side, Bálint Somogyi worked solely on this project as an MSc and later on as a PhD student. Furthermore, Márton Vörös and Viktor Ivády also contributed to this work as a PhD student. In the preparation phase of the semiconductor QDs we part-time employed laboratory assistants (István Balogh, Éva Fischer, Bence Lázár). In our collaborative research project, many other scientists in Wigner RCP (László Bencs, Károly Lajos Varga, Gábor Bortel, Attila Németh, Edit Szilágyi, Zsolt Szerkényes, Katalin Kamarás, Lajos Pogány, Miklós Veres) participated in the research, where Zsolt Szekrényes played a crucial role in the analysis of semiconductor nanoparticles. In addition, Gergely Róna, László Buday and Beáta Vértessy from the Institute of Enzymology contributed to this research as well as Zsolt Czigány from the Institute for Technical Physics and Materials Science. We also collaborated with the group of János Erostyák at the University of Pécs from 2015. We involved a number of students in this research project also as a part of their education. We summarize these efforts in Section iv. In summary, this research project generated cooperation between partners with different expertise that made it truly multidisciplinary, and it contributed to start a new “school” on physical-chemistry of semiconductor nanoparticles by training students on complex physical and chemical preparation processes and characterization at Wigner RCP.

iii. Scientific results and their impact

We carried out combined experimental and theoretical studies on the luminescent centers of silicon carbide (SiC) and SiC nanoparticles (NPs) as luminescent molecular-sized SiC NPs can be considered as ideal biomarkers [1,2]. Particularly, in the beginning of the research we carried out screening of point defects exhibiting infrared emission in small SiC NPs that is desirable for *in vivo* bioimaging. We found that either molybdenum, tungsten or vacancy-related point defects are good candidates [1]. On the other hand, we were able to produce luminescent SiC NPs already in 2011 [3] (before the start of the project) that yielded a broad visible luminescence without introducing any point defects into SiC. We suspected from our previous calculations [4] that this luminescence originates from the surface groups of the SiC NPs. Beside understanding the broad visible luminescence, detailed knowledge on the surface groups and ligands is of prime importance because these SiC NPs should be functionalized, in order to label targeted (bio)molecules. Furthermore, the surface termination may influence the biocompatibility of the SiC NPs. These investigations require large number of samples, therefore, the yield and reproducibility of the samples should have been improved compared to the existing methods in 2011. Thus, our research project had three main directions: a) Development and improvement on the production of SiC and SiC NPs, b) manipulation and characterization of SiC NP surfaces and their effect on the optical and other properties, c) identification, characterization and introduction of point defects acting as emitters in SiC and SiC NPs. The results are grouped by following these categories.

a) We developed our infiltration technique to produce large SiC particles from carbon and silicon sources. These made possible to introduce additional precursors in the process that were originally intended to employ doping of SiC particles.We developed a method to increase the yield of SiC NPs.

We used a closed acid reactor in order to well control the pressure and temperature of acidic reactions that were applied to form porous SiC as a first step in the preparation of SiC NPs. These results were published in the *Journal of Materials Research* [5]. This technique was used to fabricate our samples. Further processing (such as ion-implantation, etc.) is described below in section c).

b) As the optical properties of SiC NPs play a key role to achieve one of our specific aims we describe it in detail below. Bulk SiC is a ceramic and also acts as a wide band gap semiconductor. Its cubic form has an indirect band gap of about 2.4 eV. Thus, pure cubic SiC (3C-SiC) has only a weak absorption in the blue region and has a band edge luminescence in the green. SiC nanomaterials, however, show strong luminescence in a broad spectrum depending on its size, shape and surface termination. Our past *ab initio* calculations imply that a simple quantum confinement model with realistic SiC NP surface termination would result in ultraviolet (UV) emission (1-3 nm NP diameter) [6], however, oxygen-related groups could lead to visible luminescence [4]. Our theoretical results drove our experimental efforts for ultimate control of *both* the size and the surface of SiC NPs. We have found that our as-prepared colloid 1-3 nm SiC NPs are water soluble and exhibit stable luminescence in the blue region where the maximum of the intensity typically lies at 450 nm (~2.7 eV) and has a broad luminescence band till 700 nm [7]. Here, we were able to separate the molecular-sized SiC NPs (1-3 nm in diameter) from the larger sized SiC NPs (>6 nm) with using special filters. The composition and the size of the nanoparticles were either identified by a special NIR-AFM equipment at Katalin Kamarás group or by HRTEM at MFA (Zsolt Czigány). These results were published in *Nanoscale* [7]. The direct experimental proof on the origin of the luminescence of 1-3 nm SiC NPs has been recently achieved by engineering their surface and monitoring the change in their luminescence properties (see Fig. 1) [8]. The surface engineering was probed by surface enhanced infrared vibration spectroscopy as equipped at Katalin Kamarás group. In this study we also applied complex analysis techniques on the results of time-resolved photoluminescence spectroscopy at János Erostyák group. We could identify two major emitter groups in our 3C-SiC NPs: surface groups involving carbon−oxygen bonds and a defect consisting of silicon−oxygen bonds that becomes the dominant pathway for radiative decay after total reduction of the surface. The combined experimental and *ab initio* simulation studies could only make possible to identify these emitters by comparing the measured and calculated optical spectra. These results were published in *The Journal of Physical Chemistry* [8].

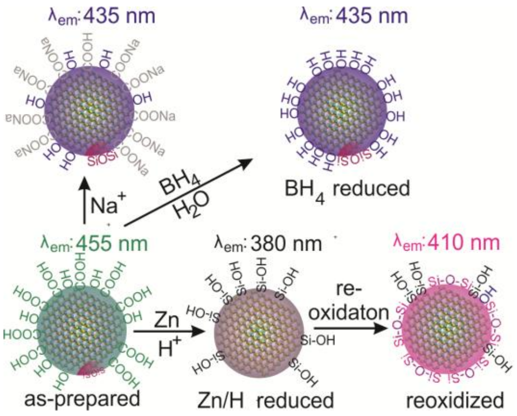

Figure 1. Surface and environment dependent luminescence of SiC NPs

Beside the surface terminations we found that the characteristic size of SiC NPs strongly affects the type of luminescence. The ultra-small 1-3 nm SiC NPs shows strong surface related luminescence whereas >6 nm SiC NPs exhibit much weaker luminescence that either originate from the band edges or stacking fault defects inside SiC NPs [7]. Recently, we have been able to produce such SiC NPs with a size of about 3-6 nm and yield strong luminescence shifted toward the red region compared to that of 1-3 nm SiC NPs. Its emission maximum is at around 530 nm and shows significant emission even at 700 nm (see Fig. 2 in Appendix B). We attribute the redshift in the PL spectrum compared to that of 1-3 nm SiC NPs to quantum confinement. Here we found here a new phenomenon. We were able to produce these 3-6 nm SiC NPs by adding Al or related precursors in the phase of producing large SiC particles. By using X-ray diffraction (XRD) and HRTEM techniques we found that the fraction of hexagonal inclusions in the 3C SiC crystal can be controlled with our fabrication method. Because the hexagonal inclusions act as blocking layers to conduction electrons that finally leads to different pore formation in the stain etching process that we apply to form SiC NPs. We provide a new theory to explain this phenomenon that can be applied to other materials where hexagonal inclusions occur in the cubic crystal. We wish to soon submit the paper about these results to *Science*. The main text of the paper is copied to Appendix B.

In addition, we found that when these SiC NPs are exposed to high pH solvents then a new photoluminescence center appears that has a maximum emission at 620 nm with a broad band up to 770 nm (see Fig. 2). This new emission is due to the change in the surface potential. Our preliminary study confirms that same type of emission can be achieved by changing the surface potential with surfactants to activate the 620-nm emission at neutral pH. These results are yet unpublished that we wish to disseminate after submission of the previous paper.

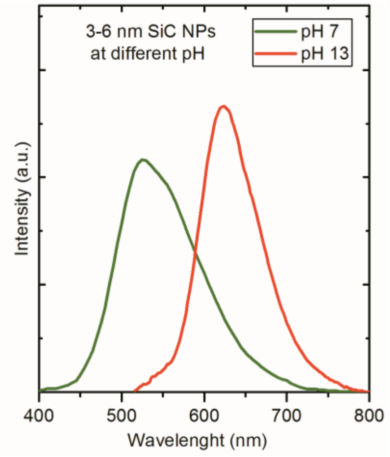

Figure 2. Fluorescence of 3-6 nm SiC NPs at different pH values of the solution

We also mention here that the manipulation of the surface termination may play a role in the biocompalibity and (bio)functionalization of the SiC NPs. The cytotoxic properties of the SiC NPs based on alamarBlueTM assay cells were studied. The presence of the SiC NPs does not affect cell growth in a wide concentration range. Two-photon excitation showed significant response from SiC nanocrystals that were injected into hippocampal CA1 pyramidal cells. The two-photon excitation study was the first proof that near-infrared two-photon excitation of SiC NPs is effective, and can be applied in biology. Our results were published in *Journal of Materials Research* [9]. In addition, we carried out a temperature dependent infrared and photoluminescence spectroscopy study, combined with *ab initio* modeling, in order to reveal the chemical transformations of the surface termination groups. We found that at temperatures above 370 K, acid anhydride groups form by condensation of water between neighboring carboxyl groups. The presence of the anhydride groups reveals the proximity of the carboxyl groups and represents a new possibility of selective engineering of new hybrid materials involving SiC NPs. The latter can be achieved by the very reactive anhydride groups that can be used to attach many types of molecules for functionalization. The results were published in *The Journal of the Physical Chemistry C* [10].

We also studied the interaction between SiC NPs and the bovum serum albumin (BSA) that is model albumin of its human form (HSA). This interaction was investigated through the quenching of BSA fluorescence lifetime and intensity in the presence of various concentrations of SiC. We carried out our measurements both in water and in PBS (Phosphate Buffered Saline) where PBS represents the ion concentration and distribution in biological environment. In PBS the so-called Smoluchowski model described the observed quenching while in water simultaneous presence of static and dynamic quenching was revealed. The dynamic quenching in both of the media is originated from Fluorescent Resonant Energy Transfer (FRET). The different behaviour of samples was explained by the structural alteration of BSA as a result of pH difference between the water and PBS dispersed samples. The acidity of the water dispersed SiC increasing rapidly, while the PBS inhibit the pH decrease in wide range of applied SiC concentration. Our calculation on the BSA-SiC system resulted in R_0=2.83 nm for the Förster radius whereas the derived donor-acceptor distance is 2.4 nm in water and 1.9 nm in PBS. We are now preparing the manuscript to publish these results.

To summarize our efforts on the manipulation of the optical properties of our SiC NPs, we found that the combination of the surface groups and the size can tune the emission wave length toward the desired near-infrared region. In this sense, our most important scientific goal has been achieved. However, the active participation of the surface groups in the emission might cause cross-correlation with its biological response. Therefore, we also attempted to introduce emitters in the SiC matrix, so then the surface of the SiC NPs may be independently manipulated from their optical signal.

c) We focused our research to find or identify near infrared emitters in bulk and nanosized SiC that may be introduced into our SiC NPs. Our strategy was to characterize and identify these emitters in bulk SiC and then to study them in NPs. Divacancy (complex of two neighbour vacancies) and Si-vacancy were already known as near-infrared emitters as well as molybdenum (Mo) and tungsten (W) related defects in SiC. We found by *ab initio* calculations that these point defects are good candidates also in small SiC NPs [1]. We further characterized Si-vacancy in SiC in international collaboration and we found that the spin properties of Si-vacancy is also very favourable that may open the door for multimodal biomarkers based on SiC NPs. This result was published in *Nature Materials* [11]. In addition, we found other very bright emitters in SiC. We could identify by theoretical simulations and group theory considerations a complex of carbon antisite and carbon-vacancy (or simply CAV defect) that can act as an ultrabright solid state single photon source operating at room temperature. This result was published in *Nature Materials* [12]. We could produce such large SiC nanoparticles in our laboratory that also showed very bright emission at room temperature, and our *ab initio* simulation identified the emitter as CAV defect. This results was published in *ACS Nano* [13]. We also found silicon-antisite related emitter in the cubic inclusion of hexagonal SiC that was published in *Nature Communications* [14]. In addition, we identified a niobium-vacancy complex exhibiting near-infrared emission that was published in *Physical Review B* [15]. We note that we attempted to dope our SiC during growth by different metals (Mo, Al) driven by our theoretical implications [1,2]. However, our PL measurements did not show change in the optical properties of SiC NPs. For the case of aluminium we developed a method to measure the Al content in our SiC NPs with using the atomic absorption spectrum (AAS) that was published in *Talanta* [16]. However, we did not find an enhanced concentration of Al in our SiC NPs that were grown in the presence of Al. Later we found that presence of Al precursor rather lead to the formation of hexagonal inclusion in 3C SiC (see Appendix B). Thus we turned our strategy and attempted to intentionally introduce vacancies at large concentration. We employed two methods to achieve this: neutron irradiation and carbon-ion implantation on our large SiC particles.

The neutron irradiation was carried out by Michael Trupke's research group (Wien Atominstitut). The radiation flux was 10^{18} n/cm^2. The energy of the neutrons was in range of 0.18 MeV to 2.5 MeV. The C+ ion irradiation was carried out in the Wigner RCP by Edit Szilágyi's group. The flux was 1×10^{15} /cm^2 and the acceleration voltage was between 200 keV and 350 keV. We found that regardless of the type of irradiation it causes significant change in the photoluminescence spectrum resulting in a strong luminescence at ca. 1.35 eV. (Figs. 3-5) where the resulted PL spectra are similar in the two types of samples (e.g., Figs. 4 and 5). All spectra were measured at 488 nm excitation. After the irradiation we used Raman-spectroscopy to identify the polytype of the SiC. The results clearly indicate that the bulk of the SiC remains cubic after bombardments (Fig. 6). To investigate the properties of the NIR-emitting point defects the samples were annealed in air at 650 C° for up to 10 hours. During this experiment we found that the intensity of the defect-related emission peak quickly decreases until we obtain the original (before irradiation) spectrum of the SiC (Fig. 7).

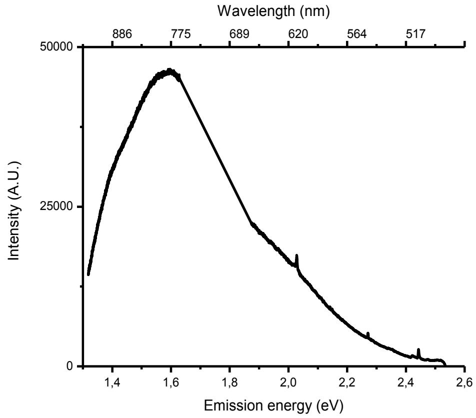

Figure 3. PL spectrum of unirradiated 3C-SiC

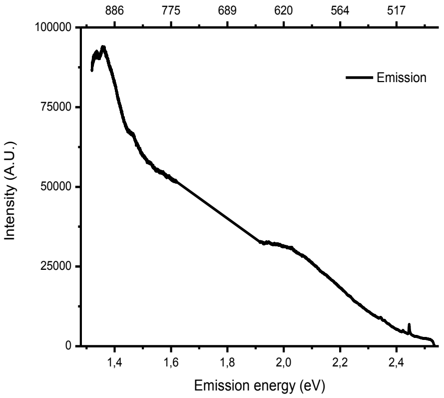

Figure 4. PL spectrum of C-ion irradiated 3C-SiC

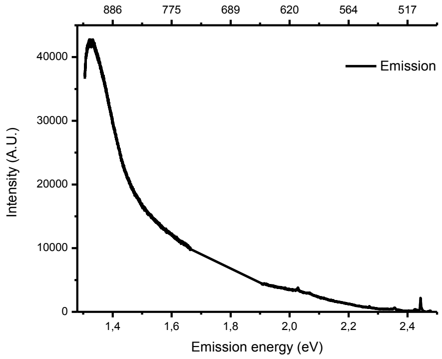

Figure 5. PL spectrum of neutron irradiated 3C-SiC

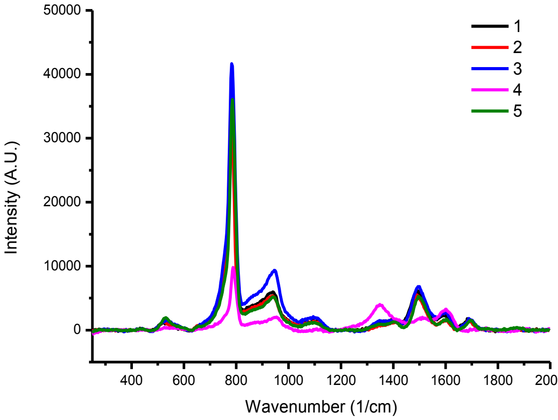

Figure 6. Raman peaks at 780-787 1/cm and 940-950 1/cm confirm that the sample is 3C-SiC

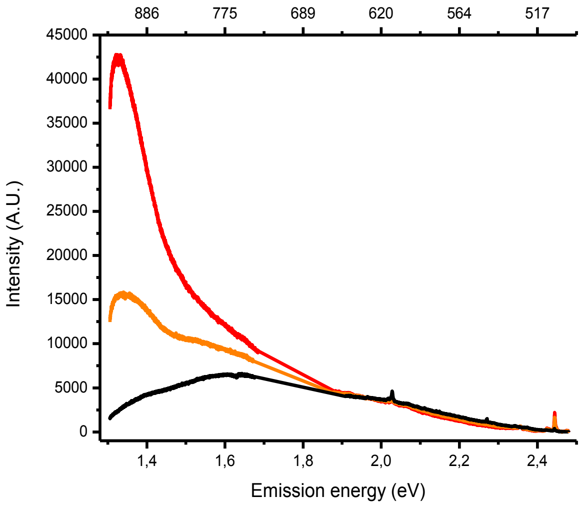

Figure 7. The emission peak at 1.35 eV (red curve) successively decreases (orange and black curves) with annealing at 650 C°

These results are yet unpublished. We still work to detect these signals in SiC NPs that are prepared by stain etching of the large SiC particles containing these near infrared emitters. Nevertheless, we may claim that we could basically achieve near infrared emission from our SiC particles.

In summary, we could prove the infrared excitation and infrared emission of SiC particles. In addition, we could prove its biocompatibility in different organic systems. We developed methods to manipulate the surface termination, in order to tune their optical properties and functionalize them. We found that the BSA only binds dynamically to SiC NPs in PBS solution. This makes SiC NPs very promising bioimaging probes. Our results were published in three *Nature* family papers, one *ACS Nano* and two *Nanoscale* papers that are premium journals in the field. The other results mostly appeared either in D1 or Q1 category journals. Besides we showed our results at national and international conferences including invited talks (see Appendix A) with great success as our presentations are often selected the best ones. Our research became clearly visible at international level. The PI of the project is a consortium leader of the Horizon 2020 collaborative research proposal on SiC based research that was evaluated as the best 24 proposals among ~840 submitted proposals in the previous FETOPEN call. We are proud that we can involve undergraduate students in the research as summarized in the next section.

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iv. Contribution to education and involvement of students in the research

Students were involved in the research of this project at various grades. **Dávid Beke** was employed full time as a PhD student from the budget of the project. The thesis points in his doctoral thesis entitled “Fabrication and characterization of silicon carbide nanoclusters” are solely based on the achieved results in the project. He plans to defend his thesis this year as he already passed the doctoral examination. ***Dávid Beke is a key researcher in the experimental group working at the level of a well-trained Postdoc researcher.*** His achievements were recognized and awarded by several institutions even at international level as listed below:

- Best presentation and publication Spring Wind Ph.D Conference (2013)
- Best Poster Awards at ACIN2013 workshop
- Wigner Traveling Grant 2013/II.
- TÁMOP 4.2.4. A/2-11-1-2012-0001, National Excellence Program, 2013-2014
- Wigner Traveling Grant 2014/I
- Research Student Bursary – E-MRS 2014
- Wigner Traveling Grant: 2014/II
- Best Presentation at György Oláh PhD Conference (2015)
- NTP-EFÖ-P15 – National Talent Program 2015
- Graduate Student Award (GSA) at European Materials Research Society Spring Meeting, Lille, May 2-6, 2016
- Wigner Traveling grant 2016/I
- Wigner Traveling grant 2016/II

- "Nemzet Fiatal Tehetségeiért Ösztöndíj" (Fellowship for Hungarian Young Talents), NTP-NFTÖ-16-0333 grant from the Hungarian Government, 2016

Particularly, I underline the Graduate Student Award at EMRS symposium that was given to award his talk entitled "Identification of Luminescence Centers in Molecular-Sized Silicon Carbide Nanocrystals" on the latest results achieved on characterization of SiC nanoparticles.

Zsolt Szekrényes participated in the research as a PhD student from Prof. Katalin Kamarás group and two thesis points of his thesis entitled "Study of complex nanostructures by infrared spectroscopy" are based on the results obtained in the project. Zsolt Szekrényes successfully graduated in 2015 as a physicist. Later on **Gyula Károlyházy** joint our research as an undergraduate student and he received his MSc as chemical engineer at the Budapest University of Technology and Economics with the diploma entitled "Fémmel adalékolt SiC nanokristályok előállítása és vizsgálata (Preparation and characterization of silicon carbide nanocrystals doped by metal elements)" in 2014. He is now a PhD student in the group working solely on the project as youth researcher at Wigner RCP. He plans to start the doctoral degree process by the beginning of next year where his doctoral thesis points will be partially based on the results achieved in the project. On the theory side of the project **Bálint Somogyi** obtained important results. He received his MSc degree in physics in 2012 entitled "Félvezető biomarkerek vizsgálata első elvű számításokkal (Study of semiconductor biomarkers by *ab initio* calculations)" and he continued as a PhD student at the Doctoral School of Physics at the Budapest University of Technology and Economics working entirely on this project. He already started the doctoral degree process and plans to defend his thesis entitled "Semiconductor biomarkers for biological imaging: A first principles study" in early 2017. He received "Publication Award" at the Department of Atomic Physics of the Budapest University of Technology and Economics in 2012 and 2014. He got a pledge at the OTDK (National competition on scientific achievements by undergraduate students) in 2013. **Viktor Ivády** contributed to identification of important color centers in SiC and understanding the properties of metal impurities in SiC that were of high importance in the project. He started his PhD in 2011 and he will defend his thesis entitled "Development of theoretical approaches for post silicon information processing" on November 11, 2016. One of his thesis points is particularly associated with the project on identification of single photon sources in SiC. In addition, **Sarolta Adél Rácz** graduated at MSc level at the Department of Atomic Physics of the Budapest University of Technology and Economics in 2016 supervised by Olga Krafcsik Homokiné with the diploma work entitled "Szilícium-karbid nanokristályok minősítése felületanalitikai módszerekkel (Characterization of silicon carbide nanocrystals by means of surface analytics tools)" where she studied our prepared SiC nanoparticles. Now she works at the Institute for Technical Physics and Materials Science HAS. Finally, **Tibor Zoltán Jánosi** from János Erostyák group defended his PhD thesis entitled "Fluoreszcens módszerek alkalmazása nanostruktúrák vizsgálatában (Study of nanostructures by means of fluorescence methods)" in 2016 where two thesis points are based on the results obtained in the project.

We involved many young students from the Faculty of Chemical Technology and Biotechnology of the Budapest University of Technology. As our project planned to employ our nanoparticles in biological systems we could attract these students from the fields of materials science and biochemistry. In one particular case (Áron Dániel Major), two BSc degrees have been achieved at the same year by the same student in these two modules. The students often participated in the research as a part of their regular education at the University in the frame of practices either during the semester ("Önálló feladat") or summer time ("Nyári gyakorlat"). Some of the students obtained BSc degree in these activities or they plan to submit their BSc work or MSc work in the next year. Beside their regular activities they came to our laboratory to carry out research in their free time, and they participated in the competition on scientific achievements by undergraduate students (TDK) at the University, or they plan to submit their work this year. **Fanni Temesváry-Kis**, **Krisztina Kalla**, **Dávid Veres** and **Roy Nor Soho** worked with us as a part of their regular education where Roy Nor Soho showed a poster entitled "Interaction of water soluble silicon carbide quantum dots with bovine serum albumin" at SIWAN6 conference (see Appendix A). Beside a list of students and their activities are provided below:

- **Klaudia Horváth**: "Szilícium-karbid nanoklaszterek fotostabilitásának vizsgálata" (Study of photostability of silicon carbide nanoclusters) (TDK work), 2014; "Szilícium-karbid nanoklaszterek fotostabilitásának vizsgálata" (Study of photostability of silicon carbide nanoclusters) (BSc, to be submitted), 2016
- **Áron Major Dániel: "**Szilícium-karbid nanoklaszterek felületének hatása az optikai tulajdonságokra" (Effect of surface in the optical properties of silicon carbide nanoclusters) (TDK work), 2014; "Szilícium-karbid nanoklaszterek redukciójának vizsgálata" (Study of reduction of silicon carbide nanoclusters) (BSc), 2014; "Szilícium-karbid nanoklaszterek pKa értékének meghatározása" (Determining the pKa value of silicon carbide nanoclusters) (BSc), 2014; "Fehérjék szilícium-karbid nanorészecskékkel való feljelölésének kidolgozása" (Development of labeling of albumin by silicon carbide nanoparticles), (MSc to be submitted), 2017
- **Dániel Unyi:** "Fluoreszcens szilícium-karbid kvantumpöttyök felületmódosítása" (Modifying the surface of fluorescent silicon carbide quantum dots) (TDK work, to be submitted), 2016
- **Balázs Juhász:** "A szilícium-karbid nanorészecskék aggregációja szerves savak jelenlétében" (Aggregation of SiC nanoparticles in the presence of organic acids) (TDK work, to be submitted), 2016
- **Fanni Oláh:** "Szilícium-karbid nanoszerkezetek előállítása" (Preparation of silicon carbide nanostructures) (MSc, to be submitted), 2017
- **Boglárka Móricz:** "Szilícium-karbid nanokristályok méretszeparálása" (Size separation of silicon carbide nanocrystals) (MSc, to be submitted), 2017

In summary, two BSc and two MSc degrees were entirely based on the results of this project, and our results contributed to an additional MSc degree. Besides three (O)TDK works summarized the results of the project. Furthermore, two PhD degrees relied on the results associated with the project, and four other PhD theses will be soon finished that use the results of the project. In addition, three MSc and one BSc works as well as two TDK works will be submitted this year or next year that are solely associated with the results of the project.

v. Outreach of the project

Beside the rise of a new "school" on preparation of semiconductor nanoparticles at Wigner RCP, the PI has reorganized and developed the laboratories that contribute to the fabrication of samples and their manipulation by chemistry, annealing, and so on. The PI founded the Wigner Advanced Materials Integrated Laboratory (Wigner ADMIL) that was supported by infrastructural grant of the Hungarian Academy of Sciences in 2015, and was registered in the list of national scientific infrastructures [http://wigner.mta.hu/admil/]. The scientific work and achievements in this project contributed to the foundation of this open-access laboratory.

Appendix A: list of presentations associated solely with the results of the project

Presenter: Ádám Gali
Invited Talk:
E-MRS Fall Meeting and Exhibit, Warsaw (Poland), (2016), Theoretical investigation of nanostructures

Talk:
SIWAN6 workshop, Szeged (Hungary), (2014), Silicon Carbide Quantum Dots: new type of light emitting nanostructure

Presenter: Dávid Beke
Talks/Seminars

- XIX International Summer School Fluorescent Nanoparticles in Biomedicine (2012) (***invited***), Miraflores de la Sierra, Madrid (Spain): Fluorescent Silicon Carbide Quantum Dots for Bioimaging And Sensing

- SIWAN5 Szeged (Hungary), (2012), Luminescent Silicon Carbide Quantum Dots Prepared by Reactive Bonding and Subsequent Wet Chemical Etching: Characterization and Potential Applications

- Francelab Tudományos Napok, Budapest (Hungary), (2013), Lumineszcens szilícium-karbid kvantumpöttyök: jellemzés és lehetséges alkalmazások

- Tavaszi Szél Konferencia, Sopron (Hungary), (2013), Lumineszcens Szilíciumkarbid Kvantumpöttyök előállítása és jellemzése

- NanoValid Training and Workshop, Zaragoza (Spain), (2013), Luminescent Silicon Carbide Quantum Dots

- Seminar, University of Pécs, Pécs (Hungary), (2013), Szilíciumkarbid Nanoklaszterek helye a biológiai alkalmazásban

- Tavaszi Szél Doktoranduszi Konferencia, Debrecen (Hungary), (2014), Szilíciumkarbid kvantumpöttyök időfelbontásos lumineszcenciaspektroszkópiás vizsgálata,

- Seminar, University of Pécs, Pécs (Hungary), (2014), Szilíciumkarbid kvantumpöttyök vizsgálata időfelbontásos lumineszcencia-spektroszkópiával

- 1st Innovation in Science, Szeged (Hungary), (2014), Silicon Carbide Quantum Dots as a Non-toxic Probe for Bioimaging: Synthesis and Application,

- Seminar, University of Pécs, Pécs (Hungary), (2014), Szilícium-karbid optikai tulajdonságait meghatározó paraméterek

- E-MRS Spring Meeting and Exhibit, Lille (France), (2014), Silicon Carbide Quantum Dots: Properties and Application

- Seminar, University of Pécs, Pécs (Hungary), (2014), Szilíciumkarbid kvantumpöttyök felületi csoportjainak a lumineszcenciára gyakorolt hatásának vizsgálata időkorrelált spektroszkópiai módszerekkel

- MRS Fall Meeting, Boston (USA), (2014), Surface Dependent Optical Properties of Silicon Carbide Quantum Dots

- Oláh György Doktoranduszi Konferencia, Budapest (Hungary) (2015), Szilícum-karbid alapú nanoklaszterek előállítása és jellemzése

- E-MRS Spring, Lille (France), (2016), Identification of Luminescence Centers in Molecular-Sized Silicon Carbide Nanocrystals

- ELFT Fizikus Vándorgyűlés, Szeged (Hungary), (2016), SiC nanokristályok optikai tulajdonságainak feltérképezése

Posters:

- MRS Spring Meeting, San Francisco, USA (2012), Luminescent Silicon Carbide Quantum Dots Prepared by Reactive Bonding and Subsequent Wet Chemical Etching

- Oláh György PhD konferencia 2012 Budapest, Hungary, Silicon Carbide Quantum Dots for bioimaging and Sensing

- ACIN2013 Namur, Belgium (2013), Preparation of small silicon carbide quantum dots by wet chemical etching

- Oláh György Doktori konferencia, Budapest, Hungary (2014), Szilíciumkarbid-alapú festékpróbák

- FQDots14, Oxford, UK (2014), Surface-Dependent Optical Properties of Silicon Carbide Quantum Dots

- SIWAN6, Szeged, Hungary, (2014), Time-Resolved Luminescence Spectroscopy of Silicon Carbide Quantum Dots

Presenter: Gabriella Drávecz

Gabriella Dravecz, Dávid Beke, Tibor Z. Jánosi, János Erostyák, Ádám Gali: Interaction between Bovine Serum Albumin and Silicon Carbide nanocrystals investigated by optical methods, Athene's Chemistry, 2015. November 27., Budapest, poszter előadás (Best Poster Prize)

Dravecz Gabriella, Bencs László, Beke Dávid, Gali Ádám: Alumínium szennyezőanyag meghatározása Szilícium-karbid nanokristályban, Magyar Kémikusok Egyesülete 2. Nemzeti Konferencia, Hajdúszoboszló, 2015. augusztus 31.-szeptember 2., poszter előadás (poster)

Dravecz Gabriella, Beke Dávid, Szekrényes Zsolt, Gali Ádám: Szilícium-karbid nanokristály és BSA fehérjemolekula közti kölcsönhatás vizsgálata, Magyar Kémikusok Egyesülete 2. Nemzeti Konferencia, Hajdúszoboszló, 2015. augusztus 31.-szeptember 2., szóbeli előadás (talk)

Dravecz Gabriella, Jánosi Tibor Z., Beke Dávid, Erostyák János, Kamarás Katalin, Gali Ádám: Szilícium-karbid nanokristály és BSA fehérjemolekula közti kölcsönhatás vizsgálata, Magyar Fizikus Vándorgyűlés, Szeged, 2016. augusztus 24-27., poszter előadás (poster)

Presenter: Gyula Károlyházy
SIWAN6, Szeged (Hungary), (2014), Preparation of doped silicon-carbide quantum-dots (poster)

ELFT Fizikus Vándorgyűlés, Szeged (Hungary), (2016), Ponthibák szabályozott előállítása szilícium-karbidban (poster)

ELFT Őszi Anyagtudományi Iskola, Mátrafüred (Hungary), (2014), Fém-adalékolt SiC kristályok előállítása és vizsgálata (talk)

Presenter: Áron Dániel Major
SIWAN6, Szeged (Hungary), (2016), Chemical reduction of SiC surface (poster)

Presenter: Klaudia Horváth
XXI. Bolyai Konferencia, Budapest (Hungary), (2016), Szilícium-karbid tartalmú rendszerek fotokatalitikus aktivitásának vizsgálata (poster)

ELFT Fizikus Vándorgyűlés, Szeged (Hungary), (2016), Szilícium-karbid tartalmú rendszerek fotokatalitikus aktivitásának vizsgálata (poster)

Presenter: Dániel Unyi
ELFT Fizikus Vándorgyűlés, Szeged (Hungary), (2016), Fluoreszcens szilícium-karbid kvantumpöttyök felületmódosítása szabályozott aggregációval (poster)

Appendix B: copy of the unpublished research paper

Controlling the size of nanoparticles at the nanoscale by engineering polytype inclusions at the microscale

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[2]Faculty of Chemical Technology and Biotechnology, Budapest University of Technology and Economics, H-1111 Budapest, Hungary

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Abstract: Production of semiconductor nanoparticles with high yield and tight control of shape and size distribution is an immediate quest in diverse area of science and technology. Electroless wet chemical etching or stain etching of semiconductors can produce semiconductor nanoparticles with high yield but usually suffers from broad size distribution. Despite stain etching is applied to many types of semiconductors, the lack of understanding the physical processes stems to optimize this technology, in order to manipulate the size dispersion of the fabricated nanoparticles. Here we report size control of silicon carbide nanoparticles of diameter below ten nanometers prepared by stain etching with varying the amount of hexagonal inclusions in cubic silicon carbide microcrystal which is a bioinert and technologically mature semiconductor. We developed a new model for the basic physical processes of stain etching of semiconductors that explains the experiments. Our model provides a recipe to engineer patterned semiconductor nanostructures for a broad class of materials.

One Sentence Summary: Based on our newly developed model on stain etching of semiconductors we demonstrate the size control of wide bandgap semiconductor nanoparticles.

A simple and robust technology is much sought-after to fabricate molecular-sized semiconductor nanoparticles (NP) with large yield(*1*). The wet chemical etching top-down technique for creating NPs form their bulk crystalline counterpart is a simple and cheap method(*2*, *3*), however, the tight control of the size of the resultant NPs after etching is very critical as the size of the NPs may affect their physical and chemical properties. In top-down technique one can readily manage the material properties at the macroscopic level, however, producing NPs from macroscopic material is usually very energy consumptive. Electrochemical etching is a promising tool for the synthesis of NPs with narrow size distribution. Even though precise size and shape control by electrochemical etching was developed for small(*4*) and large(*5*) Si particles, these methods suffer from limited applicability and expensive equipment. Electroless wet chemical etching or stain etching has very similar chemistry(*3*, *6*) and can be applied practically on any form of the material without the need of doping or introducing an external electric field. However, the chemical and physical processes in stain etching are poorly understood that stems to employ this simple technique in wide range of semiconductors.

Below we present a model to explain stain etching for a broad class of wide bandgap semiconductors that argues that, principally, it is an electrochemical process with involving a two-step oxidation and reduction mechanism (Figure 1A) where both the conduction band (CB) electrons and the valence band (VB) holes of the crystalline semiconductor play an important role. As a consequence, the size of the NPs prepared by stain etching can be controlled by varying the band edges of the semiconductor crystal with well-chosen structural defects (Figure 1B).

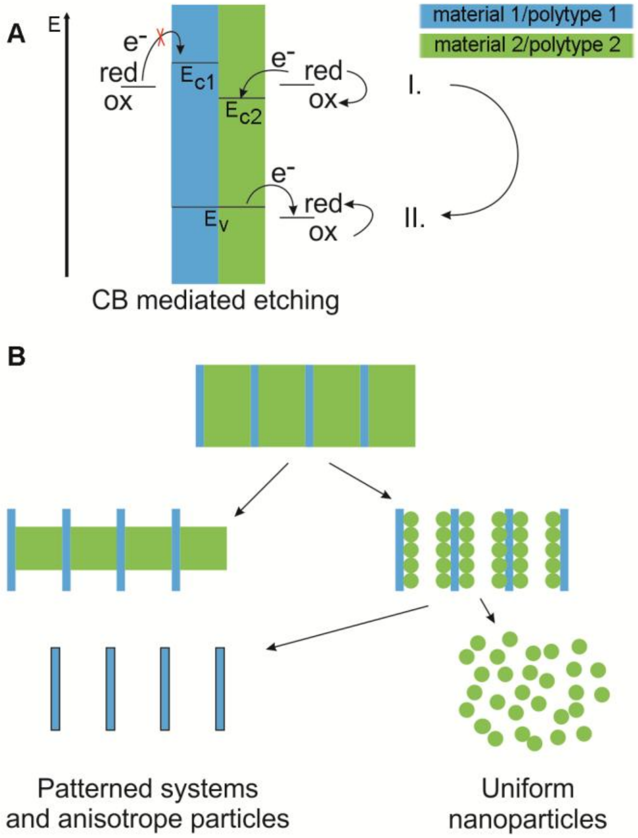

Fig. 1. Two-step model for stain etching of semiconductors mediated by the conduction band (CB) minimum. (**A**) semiconductor with "lower" CB energies can be selectively etched in a CB mediated electrochemical etching process where strong oxidant generation or surface bond weakening can occur when electron is injected to the CB. (**B**) Etching an alternating system can produce many different nanostructures like patterned wires, anisotropic or monodisperse particles

We demonstrate this effect on silicon carbide (SiC). We developed a technique to synthesize cubic SiC (3C-SiC) powder with varying hexagonal inclusions then we applied stain etching on these SiC powders and studied the properties of the resultant SiC NPs (see Methods and Materials in Supplementary Materials). The hexagonal inclusions are stacking faults (SF) in cubic SiC that form hexagonal polymorphic or polytypic mini crystals. We emphasize that the hexagonal inclusions do not alter the inherent chemical bonding of the cubic morphology. These hexagonal polytypes have the VB maximum (VBM) at the same energy within 0.05 eV but their CB minimum (CBM) lies about 0.6-0.9 eV higher than that of the cubic SiC depending on the density of the hexagonal inclusions (see Supplementary Materials). Figure 2 shows the size distribution and optical properties of SiC NPs that were prepared from SiC powder of 8% (sample I) and 15% (sample II) SF fractions (fig2 A), respectively. SiC NPs made from SiC with less SFs are in the range of 1-4 nm and had size independent emission at around 450 nm(*7*). SiC NPs that were produced from cubic SiC with higher SF fraction contain 4-6 nm particles at significant extent (Figure 2B-C). The solution containing larger SiC NPs shows a redshift in the luminescence (Figure 2D) as a consequence of the quantum confinement effect that occurs in the region of this size distribution of SiC NPs (*7*). This finding clearly demonstrates (see also Figure S1 in the Supplementary Materials) that the size of the SiC NPs can be controlled by varying SF fraction, i.e., polytype inclusions in the SiC microcrystal.

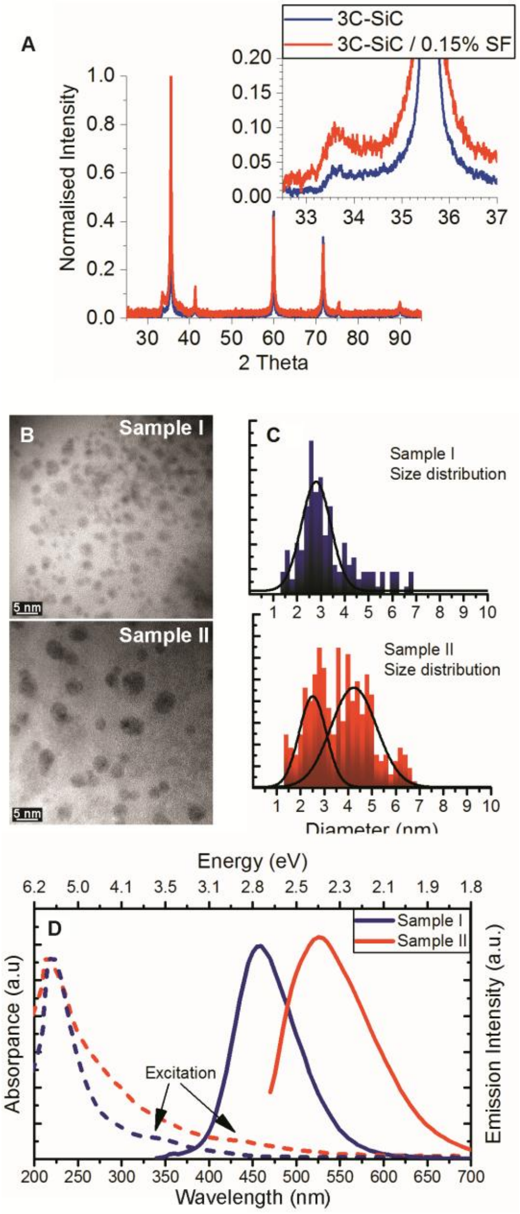

Fig. 2. Characterization of SiC particles. (A) X-ray diffractogram of cubic SiC and cubic SiC with hexagonal inclusions that are stacking faults (SF). Cubic SiC is also labeled as 3C-SiC. (B) TEM images of nanoparticles made from cubic SiC (sample I) and cubic SiC with hexagonal inclusions (sample II). (C) Size distribution of sample I and sample II. Sample II made from SiC with hexagonal inclusions contains significant fraction of particles with size around the exciton Bohr radius of about 5 nm. (D) UV-VIS absorption and emission of SiC nanoparticles made from pure cubic SiC (sample I) and cubic SiC with stacking faults (SF), i.e., hexagonal inclusions (sample II). Sample II contains larger particles therefore the luminescence is red-shifted (*8*).

Stain etching of wide bandgap SiC results in pore formation on the etched surfaces that allows NP synthesis from them(*9*, *10*). Whereas hole injection is anticipated as the driving process behind the pore formation, the redox potential of etchants often lies at higher energy than the VBM of wide bandgap semiconductors that would hinder a direct reaction between the etchant and the semiconductor surface. On the other hand, many oxidants like nitric acid or hydrogen peroxide are active via multi-electrochemical reactions where reactive species are generated in solution(*11*, *12*). Based on this we envisage a two-step mechanism for the stain etching of wide bandgap semiconductors as shown schematically in Figure 1A. In the first step, the oxidation can be done by electron injection to the CB from a molecule of the etchant. This process with further transformations in the solution(*13*) can generate a strong oxidant in the solution that is able to inject holes to the VB that finally leads to an efficient etching.

Particularly, dissolution of cubic SiC was carried out in the mixture of hydrofluoric acid (HF) and nitric acid (HNO_3) that was previously found as a suitable etchant(*14*). Electrochemical potential of VBM resides at +1.5 eV vs SHE (standard hydrogen electrode)(*15*) which is fairly higher than the redox potential of nitric acid (+0.81 eV vs SHE(*13*)) is that would block the oxidation so the pore formation of cubic SiC. However, according to our proposed two-step mechanism, the efficient etching can occur as follows. Nitrosyl ion (NO^-), that generated in the solution(*11*, *16*), is a very reactive species and the redox potential of NO^-/NO is around -0.8 eV that is above the CBM energy of cubic SiC. Thus, NO^- is ionized to neutral NO at SiC surface. We note here that the reductive nature of NO^- was already demonstrated by rapid Cu ion reduction(*17*). The resultant NO radicals can react in $HF:HNO_3$ solution by numerous way including the process like $2NO/N_2O$ that has such redox potential (+1.6 eV) that oxidizes SiC (Figure 3).

Our model explains the experimental fact that the hexagonal polytypes of SiC are resistive against $HF:HNO_3$ stain etching unlike the cubic polytype SiC despite their same chemical Si-C bonds. In the most common hexagonal polytypes, so called 6H and 4H (see Supplementary Materials), their CBM energies lie at 0.2 eV and 0.5 eV higher, respectively, than the redox potential of NO^-/NO does (see Figure 3A). As a consequence, NO radicals are hindered to form so the oxidation process is not activated. The polytype selective stain etching process has implications in the pore formation of SiC containing hexagonal inclusions that we discuss below.

The hexagonal inclusions in cubic SiC form 4H or 6H mini bands that act as blocking layers for CBM electrons that play a key role in controlling the size of the pore during stain etching. When a semiconductor is immersed in an electrolyte system, band bending takes place to equilibrate the Fermi potential. Band bending at the nanoscale is size dependent and as the particle size decreases band bending decreases as well that slows down the electrochemical reaction. Below the size of the exciton Bohr radius band bending stems the etching(*18*). In other words, a certain crystalline size is needed for migration of electrons and holes, in order to develop a depletion layer caused by band bending effect (figure 3B). Pore wall in the porous layer can be described as interconnected particles. As long as those particles connected evenly to each other, electron and hole migration is possible and band bending is realized. When the particles are separated or the migration of carriers is hindered then band bending depends only on the size of the separate particles. In this situation, the final particle size during the etching is determined by the exciton Bohr radius(*19*, *20*). As the migration of the electrons is blocked by the hexagonal inclusions in cubic SiC, the resultant diameter of the SiC NPs should be around the twice of the exciton Bohr radius which is about 5 nm (Figure 3C). Indeed, SiC NPs of about 5 nm are prepared from such SiC samples.

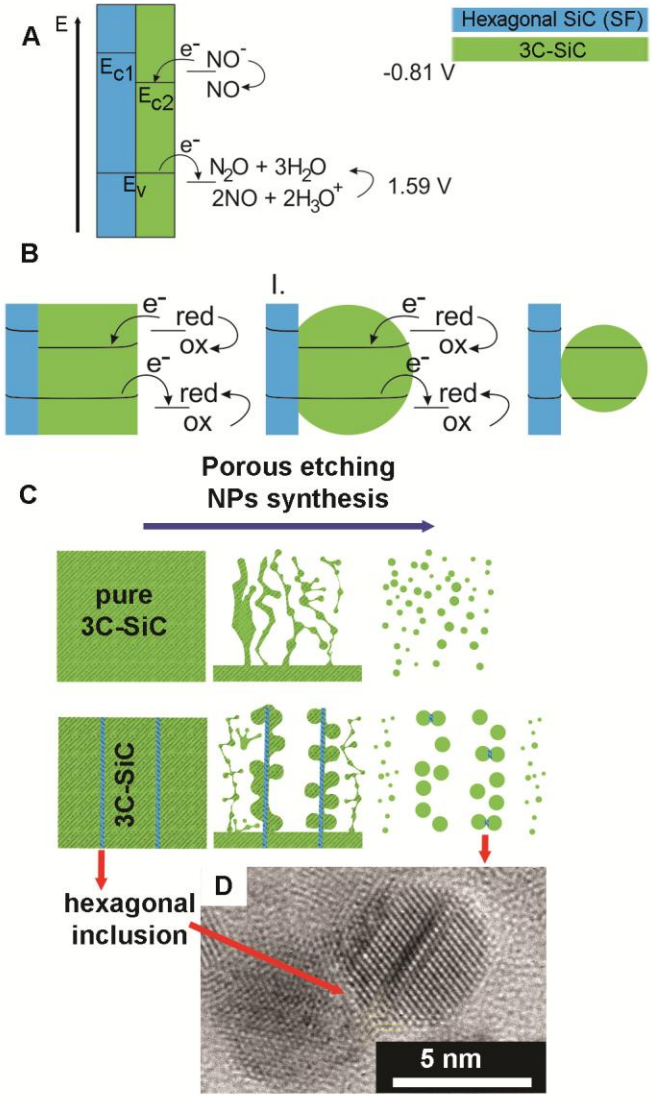

Fig. 3. The role of pore formation and nanoparticle synthesis in alternated CBMs system. (**A**) Redox reactions during SiC etching in HF:HNO3. (**B**) Size mediated electrochemical etching of semiconductors. (**C**) Pore formation and uniform particle synthesis in an alternated CBMs system. Only the lower CBM region can contribute to the pore formation. (**D**) Transmission electron microscope image of two particles connected with hexagonal inclusion. The hexagonal inclusions in SiC are nearly two-dimensional layers that contribute to the uniform size synthesis. When two particles were formed by the etching process in the opposite side of the SF then the particles are not separated after grinding.

The alternation of CBM with polytype inclusions in SiC nanowires (NW) results in nanowhiskers[17] where the polytype dependent stain etching can be employed to form patterned nanostructures (Figure 1B). Polytypism is known for many other compound semiconductors. Particularly, during the growth of semiconductor NWs polytype inclusions were identified. These polytype inclusions alter the CBM energies similarly to the polytypes of SiC. Our model on stain etching provides a method to find suitable etchants that have such redox potentials that fall between the CBM energies of the corresponding polytypes, in order to realize polytype selective etching. This effect leads to the formation of patterned nanostructures or NPs. In Figure 4 we plotted the VBM and CBM energies of technologically important semiconductors that exist in different polytypes (at least, in the form of NWs) and suitable for CB selective etching. Our model reveals that HNO_3 etchant may selectively etch the different polytypes of GaN. For other materials different etchants may be chosen where the preselection is based on the corresponding redox potentials (see the database at ref(*21*)).

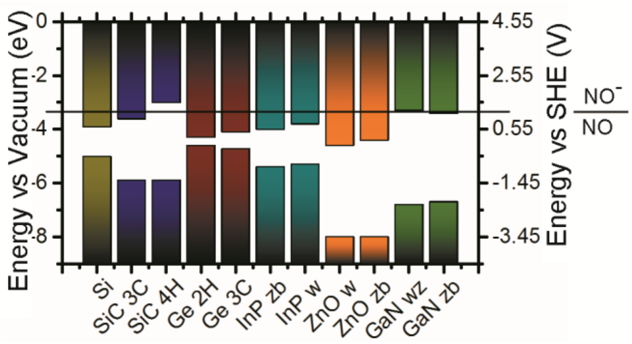

Fig. 4. Alignment of the redoxi potential for semiconductors Band diagram of semiconductors with different polytypes where the horizontal line represents the level of standard hydrogen electrode (SHE) of the redoxi potential of NO/NO$^-$ which is strong reducing agent in HNO_3 etchant(*22*). References on the data of band edges can be found in the Supplementary Materials.

Our model on stain etching of semiconductors can be employed to produce patterned NWs from technologically mature semiconductors that are applied in diverse area such as chemical and electrical sensors, photovoltaics, or quantum electronic devices(*23*) that accelerates the scientific research and technological advance in wide range of fields. In addition, we demonstrated on bio- and hemocompatible SiC NPs(*24*, *25*) that the size distribution of NPs can be tailored at the nanoscale by engineering the electron blocking layers at the microscale in the stain etching process which has high yield and is a simple method to fabricate NPs.

We acknowledge the Hungarian OTKA support for the project Nos. K101819 and K106114. DB and AG wrote the manuscript. DB and GyK prepared the SiC microcrystals. ZsCz carried out the transmission electron microscope measurements. DB prepared the SiC nanoparticles by etching. GB recorded the X-ray diffraction data and analyzed them. KK supervised the photoluminescence measurements. AG conceived and supervised the entire scientific project. All authors commented the manuscript and have given approval to the final version.

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